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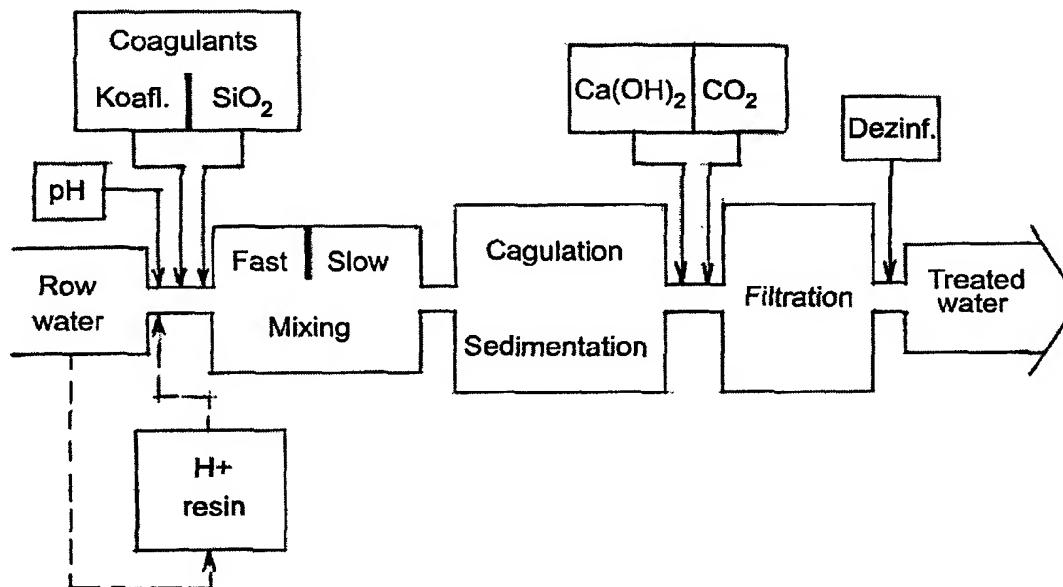
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(54) Title: METHOD FOR TREATMENT OF WATER CONTAINING HUMIC MATTER FOR THE PRODUCTION OF DRINKING WATER WITH ENHANCED COAGULATION STAGE USING INORGANICS POLYMERS OF AL AND ACTIVATED SIO2



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(57) Abstract: The invention relates to a method of removal of humic matter from natural water to drinking water quality standards in which inorganic polymers of Al and activated SiO₂ in a controlled pH range are used in a coagulation step. With this method maximum effects of reduction of humic water with minimum consumption of the chemicals and extremely low content of residual Al in drinking water is obtained.

5 **METHOD FOR TREATMENT OF WATER CONTAINING HUMIC MATTER FOR
DRINKING WATER, WITH ENHANCED COAGULATION STAGE USING
INORGANICS POLYMERS OF AL AND ACTIVATED SIO₂ IN CONTROLLED pH
RANGE**

10

a) Field of technique to which inovation belong

This inovation belong to the field of water treatment, closer, to the field of drinking water treatment, and refers to the method for removal humic matters from natural water which present 15 most wide sprad of organic pollution of natural water on broad area. Coagulation and separation processes, as one of the more representing methods for removal of humic matter from natural water are realized today by using different coagulants with partial success. The main problems are in the domain of treatment of soft and hold waters with humic matter which are very vide spread.

According to the international clasification of the patents (ICP) object of inovation is 20 indicated with basic classification symbols Cl. C 02F1/52.

b) Technical problem

The gratest problem of purification of natural waters to drinking water standards is 25 separation of humic matter, because they, amoung others, in the desinfection with chlorine give numerous halogenorganic maters with cancerogenous and mutagenous properties. For solving of this problem many methods use today, amoung others till now used dominant conventional technology of coagulation. All these technique have partial success, and there are intensive efforts for dissolving of this problem. Problems in coagulation of soft water with humic matter are 30 esspecialy pronounced. Even more pronounced problem is coagulation of this type of water in cold climate, which is a frequent case.

With this inovation important effect of the coagulation process and separation from row water of humic matter of different characteristics is obtained. With this inovation high improvement 35 in coagulation in the case of purification of soft water with humic matter, even at exstremly low temperature can be achieved.

With this inovation, from some type of row water, effect of reduction of organic matter till drinking water standard (consumption KMnO₄ smaler then 8,0 mg/l), and for water with high 40 organic content better purification results with smaller investment in the following phases of purification is obtained.

Solution in inovation is : simple, fast, effective and economic solution for removal of humic matter from row water with minimum changes in ionic content, without organic flocculant and without limitation of folowing phases purification of drinking water.

5

c) State of technic

Purification of the natural water with humic matter, for drinking water, is realised today, with several technological solutions : conventional treatment including several processes (coagulation with different schemes of flock separation), removal of humic matter on the membrane (ultrafiltration, nanofiltration and revers osmoses), oxydation with biofiltration and sorption prosesses.

In phase of purification of row water with coagulation of suspended matter and partly colloidal and dissolved organic matter are removed.

15 For coagulation different scheme of the treatment are used today, Al and Fe salts with auxiliary coagulants for treatment of different types of the water. As auxiliary coagulant activated SiO₂ and different organic polimer are used .

20 For improvement of coagulation processes new salts are sintetized, inorganic polymers giving in the water polinuclear complex hidroxo-aluminium ions with cationic properties. Type of anions in the molecul enable pollimerisation giving to it properties of flocculation matter which is very important for water difficult for flocculation.

On the west market they are : PAC, WAC, Megaflok etc., and in our country Koaflok (Patent P-551/95).

25 Great number of patented sollutions give a spectre of Al complex salts. The best, today, is the one which contains maximum homologs with 13 Al atoms in polimer, obtained by electrochemical procedure (Japan patent 24354 and 24355).

30 Unfortunately, stil special problem is presented with water containing humic matter, especiaaly soft water and coagulation in the low temperature conditions. Application of classical schemes of water treatment need enormous quantity of Al or Fe salts with low efects of purification. On the low temperatures purification of water with low ionic content with inorganic Al pollimers canot give floc, that is thet reason the existing technological schemes, having the best filters canot remove humic mater from water, as is confirmed by new data presented on the International Conference about "Removal of Humic Substances from Water" held in Norway 1999.

35 In the case of insufficient efficiency of removal of humic matter from water in addition several phases of the treatment are used: oxidation with ozone, sorption on the GAC, by that whole proccess is complicated and cost for treatment including capital cost and exploataion cost increase significantly.

Humic matter produce numerous problems in water supply (thay give colour, products of oxidation are degraded in water supply system serving as food for microbiological processes, with

5 chlorine gives many halogenorganic substances, amoung them according to new data, chlorohydroxyfuranones are extremely important mutagens), and their removal from water is one of the priority tasks. In our country bacase of complexity and high treatment costs water containing humic matter is purified only partly, or purification don't exist. With demands for limitation of content purgable of halogenorganic matter in drinking water, removal of humic matter from raw 10 water is placed as priority.

In the numerous water supply systems in our country : system for water supply on the Kopaonik, water reservoirs like Divcibare and others reduction of organic matter (consumption of KMnO₄) isn't in drinking water standard range, ground water with very high organic content like Kikinda, Zrenjanin and other are used without treatment except chlorination.

15

d) Presentation of the essence of inovation

Inovation given by this method is in great improvement of efficiency of humic matter coagulation obtained with mutual effects of two polymers, Al complex salts and activated SiO₂ in 20 favorable pH range.

The essence is in the effect of neutralization of electricity on the moleculs of humic substances with this two pollymers and entrance of humic macromolekul in stable floc and it's effective removal from water.

25 Changable content of humic matter in the natural waters of different origin, as well as changes on the water sources with time, as is the case some surface water recuire changes in the fazes of coagulation. This is obtained by the chages of content of these two polymers. This relation, expressed as Al₂O₃ : SiO₂, according to experimental results for different types of water is between 6 : 1 to 3 : 1.

30 Adaptation of relative ratio of two inorganic polymers as well as their real quantity to the type of humic matter in water is a part of the patented technology, inovation. Only good estimation of quantity and ratio of these two polimers for treated water give possibility for generation of stable floc and effective purification of drinking water, it is established as condition for application of this method.

35 Natural water with humic mater frequently have unpleasant ionic content, frequently due to shortage Ca and Mg. Adaptation of pH for optimisation of the coagulation and removal of humic matter frequently need of later neutralization with Ca(OH)₂ and CO₂, according to this conditions for improuvment of mineralization of drinking water are obtained.

Additional problem of loading of the scheme of the removal of humic matter by coagulation is high content of rezidual Al in the drinking water, and which is successfully

5 eliminated using this method, whose correct application is garant for obtaining of the most strict standards.

Inovation is tested in laboratory conditions, jar test, while only phase Al polimer application condition is tested in sity, that is giving data for conclusion about improvement effects of purification obtained by laboratory jar test.

10 In the application this method does not have special demands compared to conventional coagulation process. As for conventional system, in jar test, phases of the coagulation and sedimentation are in domain : rapid mixing with 200 r/min. (2 min.), slow mixing with 15 - 30 r/min (10 min.) and precipitation cca. 20 min. by which this phase of purification is s finished. Process on the instalation is deffined by conditions of the instalation.

15 Adjustment of optimum pH, for the greatest number of water is in the range 5.5 to 6.5 (if it is necessary), realized before coagulants dosage with some of mineral acids (H_2SO_4 , HCl or with cationic resin H^+ type), in that way with minimum changes on the ionic content, or that is all time in range of the drinking water quality standards, like this realized with $Al_2(SO_4)_3 \cdot 18H_2O$. For the natural water with low pH, type of water source on Kopaonik, adjustage of pH isn't nessesary, 20 (excluding possible changes of water quality during a year when situation expect this), and finaly neutralization will be realized with $Ca(OH)_2$ before filtration.

Dozage of the coagulant, Al polimer and activated SiO_2 is realized just before rapid mixing, and later adjustment of pH (if it is necessary) is realized after sedimentation.

25 Inorganic polymer is dosed without dissolution, or in the range of dissolution allowed by the producer, when worked with concentrated substances.

Activation of amorphous SiO_2 is realized by neutralization of alkalinity, 1,0 % solution, which imediately is diluted to 0.1 - 0.05 % solution with slow, mixing providing activity of SiO_2 for many hours use.

30 The doses of Al polimer and activated SiO_2 are deffined for a concrete case of purification and can vary in broad range, for Al polimer 2.0 - 25 mg/l Al_2O_3 and activated SiO_2 from 0.5 - more than 5.0 mg/l.

e) Short illustration of figure of the plan

35 Investigations in laboratory conditions were realized with standard methodology, by jar test with propeler mixer changable speed from 10 - 200 r/min., which provided realization of experiments in defined conditions : rapid and slow mixing.

For investigation different comercial polimer : PAC, Megafloc and Koaflok were used. Mostly experiment were realized with Koaflok.

5 Process of purification of row water by coagulation with separation floc on the instalation has phases given in the scheme 1.: Adjustment of the pH (if it is necessary), dosing of the koagulants (Al polimer and activated SiO₂) with mixing phases (rapid and slow mixing) and finally sedimentation and filtration. Adjustment of the pH before phase of coagulation (if it is necessary) is realized by dozing of mineral acids or by filtration of some part of the water flow
10 (about 15 % and more persent, depanding on expected pH and type of water) trough column with H⁺ resin. Water for acidification is taken from basic flow, row water, or after sedimentation of filtration phases protecting H⁺ rasin polution. Neutralization of treated water is realized before filtration phases.

15 The method permits other purification schems. This is related to existing instalations, for example these with coagulation/direct filtration. In this case effects of the process is dependant on concentration of humic matter, or coagulant doses, because the filter run is dependant on these parameters.

f) Detailed description of the inovation

20 To the row water, before adjustment of the pH to app 5.5 - 6.5 range (if row water isn't in this in the source), and reduction of biologic activity (in the case treatment of the surface water resources is realized, desinfection in first step if the biologic activity limit sedimentation process), inorganic polimer Al and SiO₂ is added, pass through phases of rapid and slow mixing and after 25 that removed floc by sedimentation during about 30 min, according to the standard procedure of jar test. Under the plant conditions realization of the procedure is defined by characteristics of the instalation.

30 Adjustment of the pH (for the row waters with low mineralization adjustment is realized with some of mineral acids : H₂SO₄ or HCl, but for waters with high bufer capacity where exist possibility for degradation of ionic content and water quality this realized by use of H⁺ cationic resin) for optimal effects of purification is realized on the begining of the process. Possible later corections, adjustment to range defined by drinking water standards and improvement water stability is realized after sedimentation, but before phase of filtration.

35 Efficiency of the removal of humic matter is dependant on the conditions of the procedure and for optimal conditions : doses of complex Al salts and activated SiO₂, as well as optimal pH value are defined for each case separately. For the ground water resources these values are stable, but for surface water they must be adjusted according to changes of characteristics of the treated water.

5 All process is controled by some parameters of the water quality that give data about effect of the purification : turbidity, consumption of KMnO₄, colour, uv-extincion, PTHM and residual Al concentration.

10 All results of jar tests are related to characteristics of decanted water. Only some results refered to filtered water will be pointed out.

15 By using inorganic polymer Al and activated SiO₂ as auxiliaty coagulants, by controling pH in the optimal range iprouvement of coagulation process and integral effects of purification compared to conventional treatment are obtained :

- reduction of organic matters, especialy humic matter, from water (calculated as consumption of KMnO₄ from 70 to 90 %),

15 - high percent of organic matter as uv-extintion is remuved, which is very important according to the fact that this matter is the main precursor of halogenorganic matters (effects this reduction are in special cases 90 %),

20 - process of coagulation and separation is intensified even with extremly low temperature (process coagulation and sedimentation of water on Kopaonik is realized independant of low temperature),

- it reduces content of the THM prekursors in the purified water, rarely lower to MLC in the drinking water (PTHM reduced about 90 %),

25 - it attained especially important effects in the reduction value of colour even more then 95 %,

- it attained extremely low concentration of residual Al in drinking water (for corectly performed coagulation process concentration Al is lower then 0.050 mg/l, according to this the most strict standard for drinking water quality is provided,

30 - it reduces consumption of Al salts (consumption Al is reduced for 2 to more then 5 times, compared to conventional treatment with As sulphate even with very high effects of purification, as the case of water purification from accumulation on the Divjibare, fig. 4.3.),

- it reduces effects to the environment from mud from drinking water facilities from 50 - 80 %.

All cited parameters present more effective enhanced coagulation then that postuled by US EPA (1998).

35 Presented examples of laboratory investigation illustrate this conclusions.

Example 1. Results of laboratory investigations purification effects of ground water in Kikinda

5 Row water has following characteristics : pH = 8 - 8.2, turbidity = 0.60 NTU, consumption of KMnO₄ = 28-30 mg/l, uv-ext. = 0.300 1/cm, PTHM = 350 µg/l, and CHCl₃ = 300 µg/l.

By coagulation and sedimentation according to jar test methodology with optimum doses : koaflok (15 mg Al₂O₃/l), SiO₂ (2 mgSiO₂/l) i with pH near 7.0 water of characteristics was obtained : turbidity = 0.40 NTU, consumption of KMnO₄ = 9.4 mg/l, uv-ext. = 0.076 1/cm.

10 Better effects of reduction of organic matter, consumption of KMnO₄ = 8.6 mg/l, is obtained with dosse of 10 mg Al₂O₃ at pH = 6.0. Lowering pH is limited by increasing of ionic strenght and sulphate or chloride content. Equivalent effects are obtained by ussing H⁺ cationic resin with simultaneous reduction of treated water hardness. This method need somewhat higher more investment, but it provides hardnes of the treated water in the range of drinking water quality 15 standard.

On the fig. 1.1., and 1.2., some results of depandance of degree of the reduction of organic matter (consumption KMnO₄) and uv-extincion (as parameters water quality) in function of doses koaflok are given. In full-scale conditions, with effects of filtration, expected improvement of water quality and reduction of koaflok doses of about 20 %.

20 **Example 2.** Results of laboratory investigation purification effects of ground water of Zrenjanin

Row water has following characteristic : pH = 7.7 - 8.2, turbidity = 1.5 - 2.8 NTU, consumption of KMnO₄ = 52 mg/l, uv-ext. = 0.300 1/cm, colour = 50 - 60.

25 By coagulation and sedimentation according to jar test methodology with optimum doses : koaflok (20 mg Al₂O₃/l), SiO₂ (4 mgSiO₂/l) i with pH near 7.0 water following characteristics was obtained : turbidity = 0.65 NTU, consumption KMnO₄ = 16.1 mg/l, uv-ext. = 0.144 1/cm, colour = 5 mg Pt/l.

30 Better effects of organic matter reduction were obtained by lowering pH by using H⁺ cationic resin which limited increased hardness of water. This was obtained by passing some part, about 15 % or more persent through H⁺ cationic resin with simultaneous reduction of treated water hardness. This method need more investment, but it provide of treated water hardnes in the range of drinking water quality standards.

35 On the fig. 2.1., and 2.2., some results of depandance degree of the organic matter reduction are given (consumption KMnO₄) and uv-extincion (as parameters of water quality) in function of koaflok doses.

Example 3. Results of laboratory investigation of purification effects of surface water on Kopaonik.

5 Row water has changable characteristics : pH = 5.2 - 7.5, turbidity about 0.6 NTU, consumption KMnO₄ = 8.6 - 12.7 mg/l, uv-ext. = 0.09 - 0.115 1/cm, colour = 15, PTHM = 150 - 230 µg/l, and CHCl₃ = 120 µg/l.

10 Characteristics of this water are in the low ionic content and low temperature (parameter limiting coagulation possibility) and with high specific yield THM, as defined needed degree of humic mater reduction in the case of desinfection with chlorine.

By coagulation and sedimentation according to jar test methodology with optimum doses : koaflok (3 mg Al₂O₃/l), SiO₂ (0.5 - 1.0 mg SiO₂/l) i with pH near 7.0 water following characteristics was obtained : turbidity = 0.25 NTU, consumption KMnO₄ = 4.04 mg/l, uv-ext. = 0.005 1/cm, colour = 0.5 mg Pt/l, PTHM = 65 µg/l, and CHCl₃ = 30 µg/l.

15 On the fig. 3.1., and 3.2., some results of depandance degree of the organic matter reduction are given (consumption KMnO₄) and uv-extincion (as parameters of water quality) in function of koaflok doses.

20 **Example 4.** Results of laboratori investigation of surface water effects purification from accumulation Divcibare

Row water has characteristics : pH = 7.1., turbidity about 3.0 NTU, consumption KMnO₄ = 26 mg/l, uv-ext. = 0.210 1/cm, colour = 20, PTHM = 650 µg/l, and CHCl₃ = 500 µg/l.

25 Characteristics of this water is in the low ionic content and low temperature (parameter limiting coagulation possibility) and with high specific yield THM, which defined needed degree of humic mater reduction in the case of desinfection with chlorine.

By coagulation and sedimentation according to jar test methodology with optimum doses : koaflok (3.5 mg Al₂O₃/l), SiO₂ (1.0 mg SiO₂/l) i with pH near 7.0 water of following characteristics was abtained : turbidity = 0.18 NTU, consumption KMnO₄ = 4.0 mg/l, uv-ext. = 0.005 1/cm, colour = 1.5 mg Pt/l, PTHM = 65 µg/l, and CHCl₃ = 30 µg/l.

30 **Example 4.1.** In other condition surface water from hipolimnion of this accumulation Divcibare had difrent characteristics, higher consumption of KMnO₄, higher uv-extincion and higher demand for coagulants.

Row water has had the following characteristic : pH = 7.3., turbidity about 3.8 NTU, consumption KMnO₄ = 32 mg/l, uv-ext. = 0.268 1/cm, colour = 33 mgPt/l, PTHM = µg/l, and CHCl₃ about µg/l.

After adjustment of pH to 6.0 coagulant is dozed : koaflok (9:0 mg Al₂O₃/l), SiO₂ (3.0 mg SiO₂/l). After sedimentation new adjustment of pH and rapid filttaion (9 m/h) through sand and

5 gravel (column 0.6 m high and with sand and gravel 0.6 - 4 mm) is performed water quality with : pH = 7.08, consumption KMnO₄ = 7.2 mg/l, turbidity = 0.15 NTU uv-ext. = 0.041 1/cm, colour = 2 mg Pt/l, residual Al = 0.030 mg/l is obtained.

10 On the fig. 4.1., and 4.2., some results of depandance degree of the organic matter reduction (consumption KMnO₄) and uv-extincion (as parameters water quality) in function of doses koaflok are given.

On the tab. 4.3. effectivity of reduction of dissolved organic matter (consumption KMnO₄) for different schemes of raw water purification from lake Divcibare (1-with Al sulphate, 2-with Koaflok, and 3-with Koaflok with auxiliary coagulant), obtained on the jar test is presented.

15

20

PATENT CLAIMS

1. Method for purification of natural water with humic matter to drinking water is, pointed by this, that removal of humic matter from raw water under all temperature conditions, in the acid 10 range is ensured by type of the water or by adding mineral acid or by using ionic H⁺ resin, after that treated with inorganic polymer Al and activated SiO₂ in optimal concentrations, defined in application and dependant on type of water vary in wide range (for Al polymer from 1.5 to over 20 mg/l as Al₂O₃, and SiO₂ from 0.5 to over 5.0 mg/l) that under selected conditions of coagulation 15 and separation of floc (by sedimentation, flotation or direct filtration) with adjustment of pH decanted water to the desirable range (by dose lime with or without CO₂, with or without adjustment of hardness) and with following filtration maximal reduction of the humic matter with minimal consumption of chemicals and minimum concentration of the residual Al in drinking water will be ensured.

2. Method according to demand 1 is pointed by this, that is :
20 a) in the case of soft water purification final neutralization realized with Ca(OH)₂ and CO₂ to desired pH and hardness of the water,
b) in the case of hard water purification regulation acidity is obtained by passing one part of the flux through the column with H⁺ type of resin, by this removal of significant quantity of cation is obtained and then by final neutralization the best ionic content.

25 3. Using inorganic Al polymer and activated SiO₂ as coagulants for water with humic matter purification is appointed by this that in phase of application the most favorable contents and mutual relation this two chemicals are defined for obtaining the best effects of the purification dependant of type on water or composition of humic matter which is treated.

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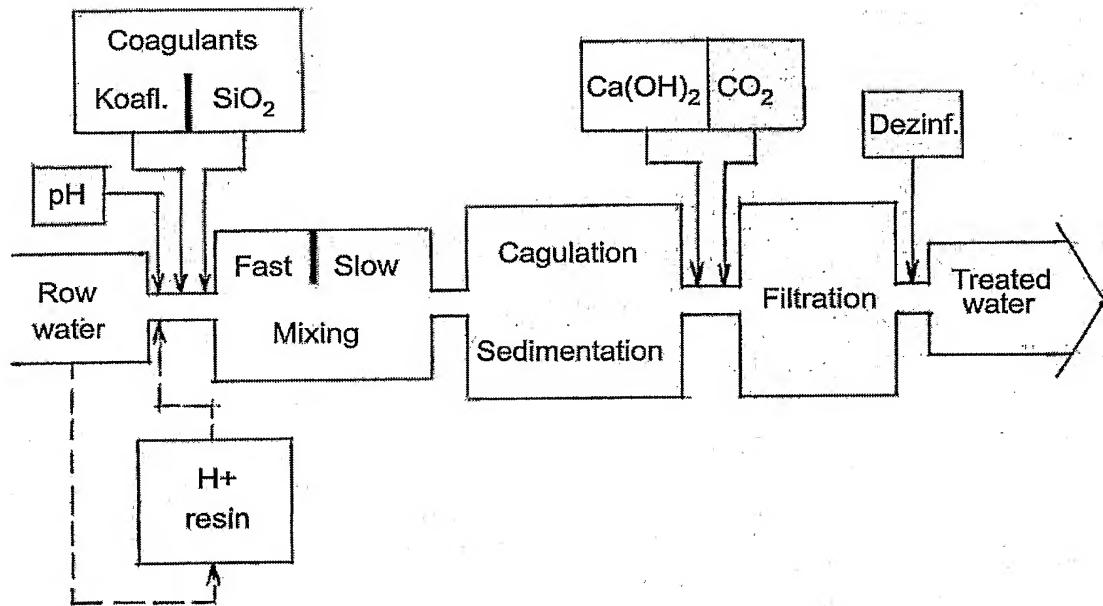


Fig. 1.

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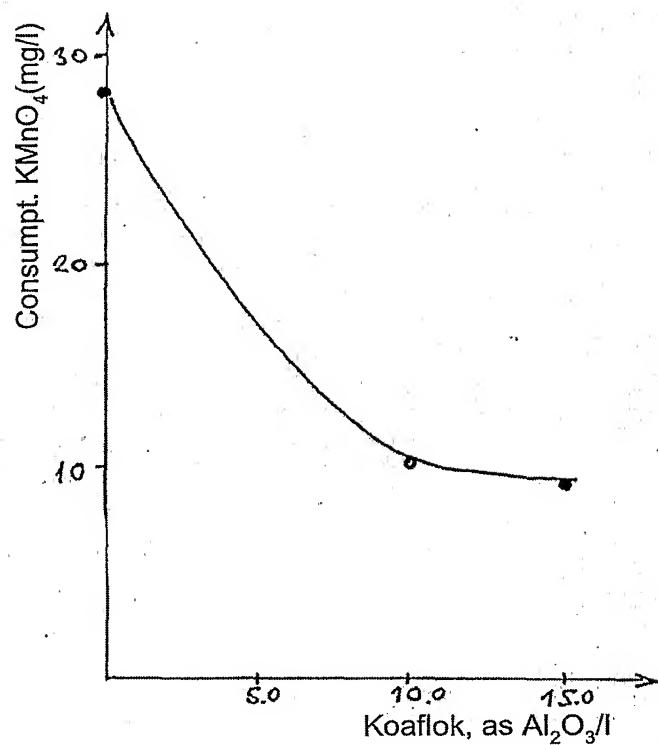


Fig.1.1.

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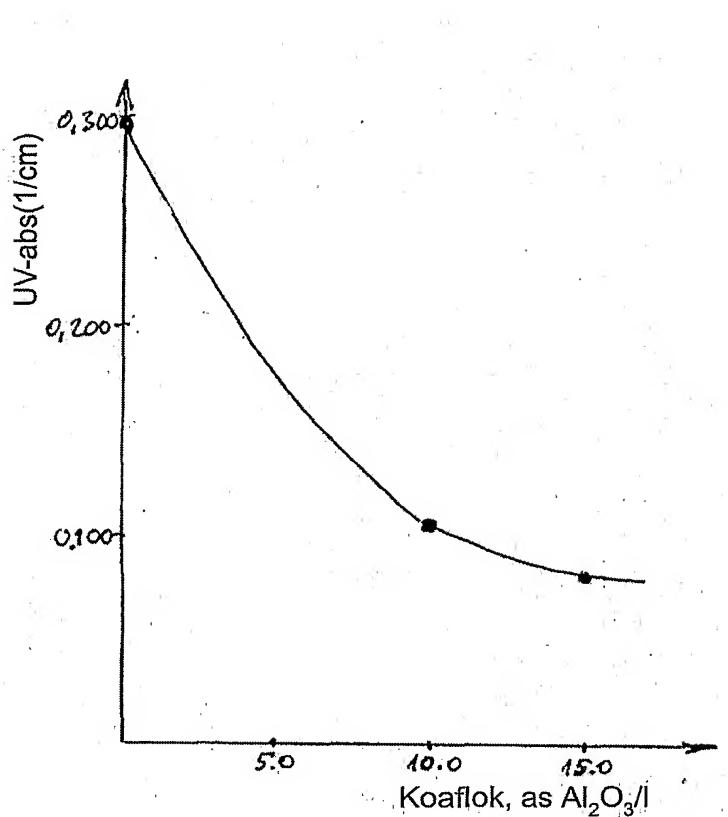


Fig. 1. 2.

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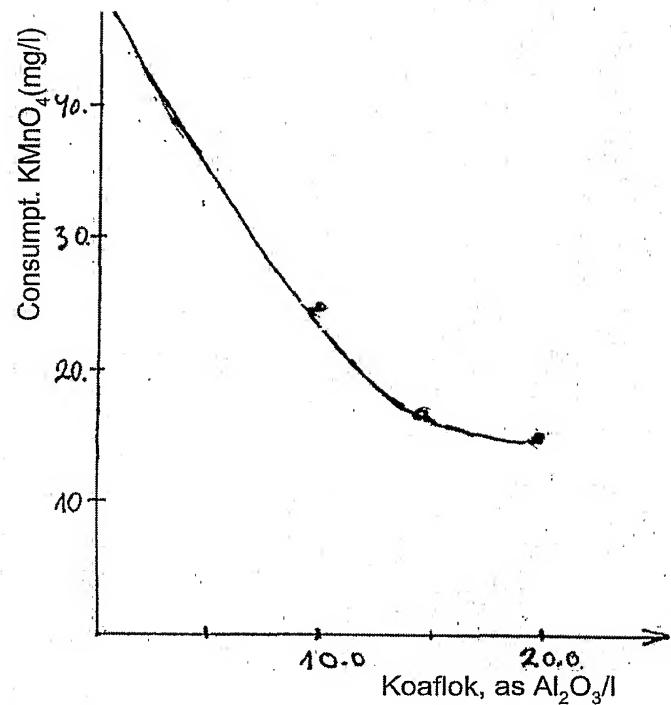


Fig. 2. 1.

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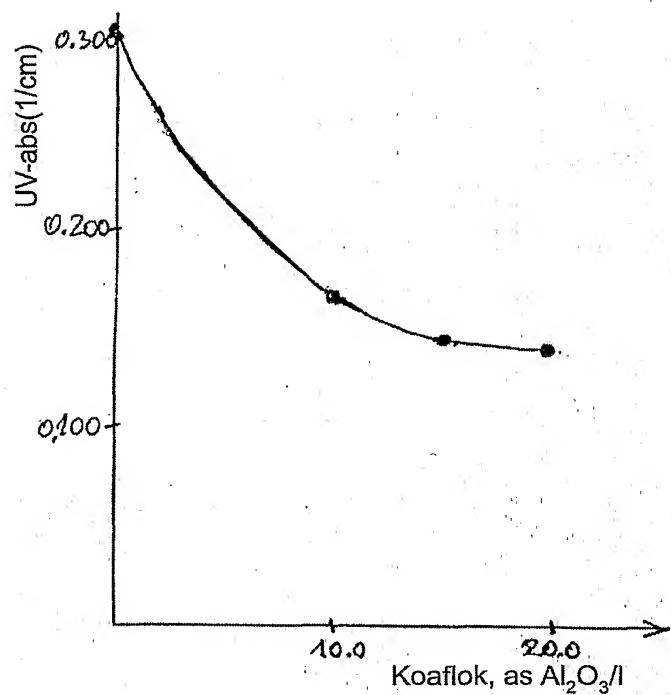


Fig. 2. 2.

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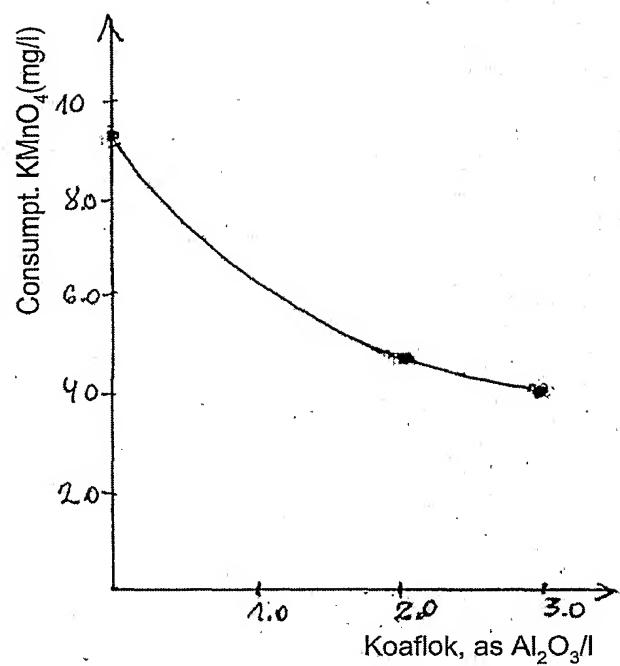


Fig. 3. 1.

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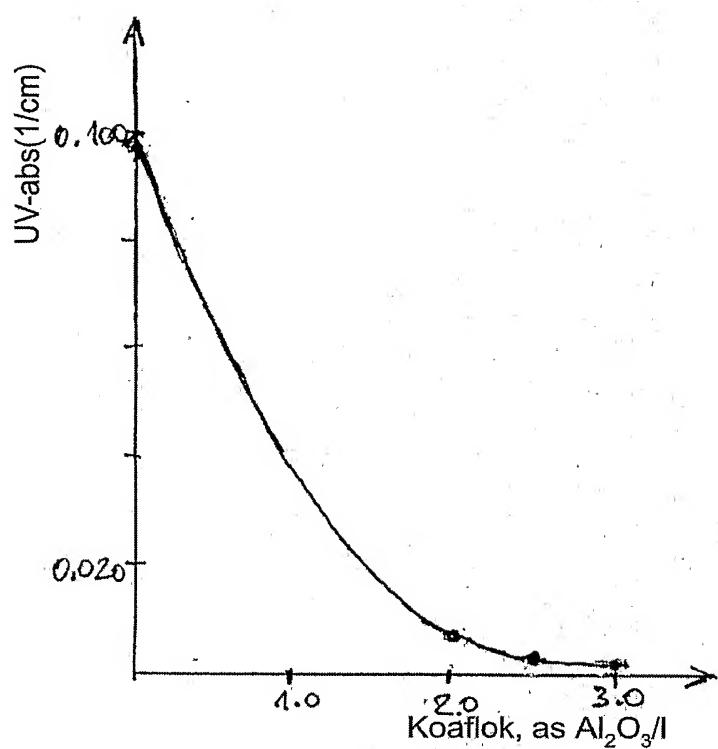


Fig. 3. 2.

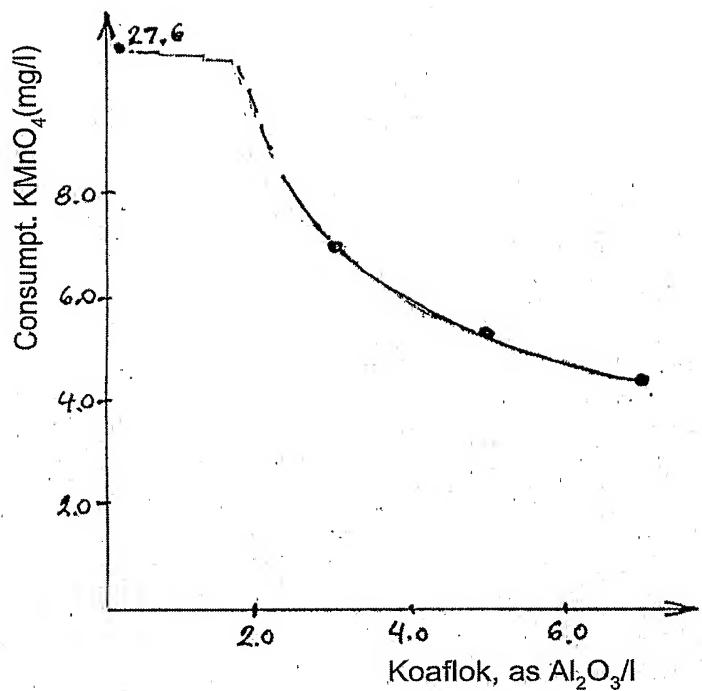


Fig. 4. 1.

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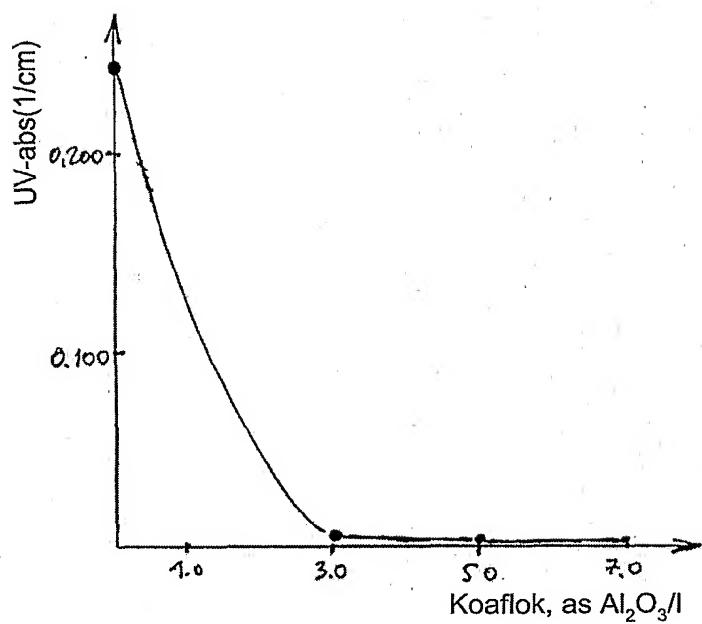


Fig. 4. 2.

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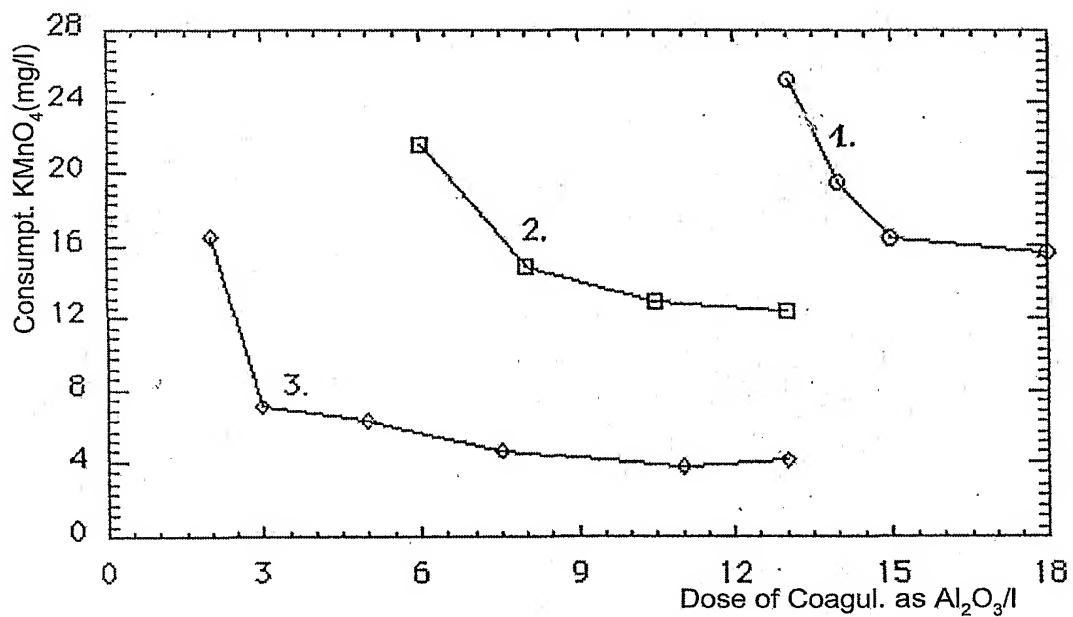


Fig. 4. 3.

INTERNATIONAL SEARCH REPORT

In...ional Application No
PCT/YU 01/00012A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 513 619 A (UGINE KUHLMANN) 1 April 1983 (1983-04-01) the whole document ---	1, 3
A	FR 2 555 980 A (HEIDENREICH JOHANN) 7 June 1985 (1985-06-07) the whole document ---	1-3
A	DATABASE WPI Section Ch, Week 199431 Derwent Publications Ltd., London, GB; Class D15, AN 1994-251942 XP002178792 & JP 06 182355 A (TAKI CHEM CO LTD), 5 July 1994 (1994-07-05) abstract ---	1-3

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Int'l Application No
PCT/YU 01/00012

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 023 012 A (BUCHAN PIETER W W ET AL) 11 June 1991 (1991-06-11) column 1, line 12 - line 17 column 3, line 20 - line 58 claims -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/YU 01/00012

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR 2513619	A 01-04-1983	FR	2513619 A1	01-04-1983
FR 2555980	A 07-06-1985	FR	2555980 A1	07-06-1985
JP 6182355	A 05-07-1994	NONE		
US 5023012	A 11-06-1991	NONE		

DERWENT-ACC-NO: 2002-106394

DERWENT-WEEK: 200667

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TITLE: Purification of natural water to give drinking water by removing humic matter involves adding mineral acid or cationic resin, treating water with coagulants, coagulating and separating floc, and filtering humic matter

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PRIORITY-DATA: 2000YU-000353 (June 6, 2000)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 0194265 A1	December 13, 2001	EN
AU 200165430 A	December 17, 2001	EN
EP 1294642 A1	March 26, 2003	EN
EP 1294642 B1	August 16, 2006	EN
DE 60122329 E	September 28, 2006	DE

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK S L TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW AL AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC MK NL PT RO SE SI TR AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC NL PT RO SE TR

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL- DATE
WO2001094265A1	N/A	2001WO-YU00012	June 1, 2001
AU 200165430A	N/A	2001AU-065430	June 1, 2001
DE 60122329E	N/A	2001DE-622329	June 1, 2001
EP 1294642A1	N/A	2001EP-939966	June 1, 2001
EP 1294642B1	N/A	2001EP-939966	June 1, 2001
EP 1294642A1	N/A	2001WO-YU00012	June 1, 2001
EP 1294642B1	N/A	2001WO-YU00012	June 1, 2001
DE 60122329E	Based on	2001WO-YU00012	June 1, 2001

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C02F1/52 20060101
CIPP	C02F1/52 20060101
CIPS	C02F1/52 20060101
CIPS	C02F1/54 20060101

ABSTRACTED-PUB-NO: WO 0194265 A1**BASIC-ABSTRACT:**

NOVELTY - Natural water is purified with the removal of humic matter to give drinking water by adding mineral acid or ionic H⁺ resin depending on the type of water; treating water with coagulants comprising inorganic polymer aluminum (1.5-20 mg/l as aluminum oxide) and activated silicon dioxide (0.5-5.0 mg/l); coagulating and separating floc; and filtering the humic matter.

DESCRIPTION - Purification of natural water to give drinking water by removing humic matter comprises adding mineral acid or ionic H⁺ resin, depending on the type of water; treating water with coagulants comprising inorganic polymer aluminum (1.5-20 mg/l as aluminum oxide) and activated silicon dioxide (0.5-5.0 mg/l); coagulating and separating floc using sedimentation, flotation or direct filtration, by adjusting the pH using lime with optionally carbon dioxide, and optionally adjusting hardness; and filtering the humic matter.

USE - For purification of natural water containing humic matter.

ADVANTAGE - The method is simple, fast, effective and an economical

solution for removing humic matter from raw water with minimum changes in ionic content and without organic flocculants. It reduces humic matter with minimal consumption of chemicals. The method provides drinking water with a minimum concentration of the residual aluminum.

EQUIVALENT-ABSTRACTS:

INORGANIC CHEMISTRY

Preferred Process: For soft water purification, neutralization is realized using calcium hydroxide and carbon dioxide until the desired pH and hardness of the water is achieved.

For hard water, the acidity is regulated by passing one part of the flux through the column with H⁺ type resin.

Preferred Function: The inorganic aluminum polymer and activated silicon dioxide provide the best effect of water purification depending on the type of water and the composition of humic matter being treated.

Ground water in Kikinda having a pH of 8.0-8.2, turbidity of 0.60 NTU, consumption of potassium permanganate (KMnO₄) of 28-30 mg/l, uv-ext of 0.300 1/cm, PTHM (sic) of 350 microg/l, and trichloromethane consumption of 300 microg/l, were purified by coagulation and sedimentation according to jar test methodology with optimum doses of Koaflok(TM) (15 mg aluminum oxide/l, 2 mg silicon dioxide/l) obtaining a pH of 7.0. The water obtained had a turbidity of 0.40 NTU, consumed potassium permanganate of 9.4 mg/l, and uv-ext of 0.076 1/cm. Organic water was better reduced using KMnO₄ of 8.6 mg/l obtained with a dose of 10 mg aluminum oxide at a pH of 6.0. The lowering of pH was limited by increasing the ionic strength and sulfate or chloride content. Equivalent effects were obtained using H⁺ cationic resin with simultaneous reduction of treated water hardness.

TITLE-TERMS: PURIFICATION NATURAL WATER DRINK
REMOVE HUMIC MATTER ADD MINERAL ACID
CATION RESIN TREAT COAGULATE SEPARATE
FLOCCULATE FILTER

DERWENT-CLASS: D15

CPI-CODES: D04-A01B; D04-A01G; D04-B04;

UNLINKED-DERWENT-REGISTRY-NUMBERS: ; 1544U ; 1694U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2002-032718